



Short communication

New concepts for process intensification in the conversion of glycerol carbonate to glycidol

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ABSTRACT

Glycerol is a major by-product in biodiesel manufacturing, which surplus raises a critical need to transform it into high added-value products. In particular, glycerol carbonate is an important glycerol derivative being the most valuable intermediate for the production of glycidol, which is an added-value product of major industrial interest used, for example, as a precursor for the synthesis of a large number of polymers. Solvent-free conventional thermal activation, ultrasound-activation and microwave-activation in the liquid phase are able to selectively transform glycerol carbonate into glycidol under mild conditions using a ZSM-5 zeolite catalyst and a zinc oxide-supported nanoscaled cobalt oxide catalyst with short reaction times and in the absence of solvent. To the best of our knowledge, we report the highest selectivity to glycidol (>99%) from glycerol carbonate at high conversion values (71%).

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1. Introduction

The biodiesel production has considerably increased in the last decade in the scenario of minimizing dependence on fossil fuels. This expansion in biodiesel manufacturing is generating large amounts of glycerol as a by-product, which price drops in the market. Therefore, there is an opportunity and a need to transform glycerol into high value-added chemicals to prevent its accumulation as a waste and improve the economy of the biodiesel industry, increasing its sustainability.

Glycerol is a versatile raw material; several conversion processes have been described in literature for the synthesis of useful glycerol derivatives [1,2]. Among these, glycerol carbonate represents an important glycerol derivative with low toxicity, good biodegradability and high boiling point. It is a bi-functional compound used as a solvent or surfactant and has many applications in different industrial sectors. Moreover, glycerol carbonate is the most valuable intermediate for the production of glycidol, which is a precursor for the synthesis of polymers. In addition glycidol is also used as a stabilizer for natural oils and vinyl polymers, as demulsifier, also used in surface coatings, and in chemical synthesis of several intermediates, pharmaceuticals and as a gelation agent in solid propellants [3,4].

Two methods are traditionally used for industrial glycidol production [5–8]. One is the epoxidation of allyl alcohol using hydrogen peroxide and a solvent in the presence of a homogeneous catalyst based on tungsten or vanadium, for example. The large number of steps required to obtain the desired product is the main disadvantage of this method, such as the extraction of glycidol from the reaction mixture. In addition, some of the catalysts used in this reaction such as tungsten decompose during the reaction, being its consumption another important factor in the final cost of the process. Later, Wróblewska and Fajdek found a heterogeneous titanium silicalite (TS-1 and TS-2) catalyst to carry out this reaction efficiently, avoiding the problems related to the recovery of the catalyst [9]. Another method to industrially produce glycidol is through reaction of epichlorohydrin with caustic [10].

However, there are only a few research groups that have investigated the synthesis of glycidol from glycerol carbonate. Malkemus and Currier were the first to patent the synthesis of glycidol from glycerol carbonate by homogeneous catalysis using a metal salt as catalyst, obtaining glycidol yields of 80–90% at high temperature (175–225 °C) and low pressure (1–100 mm of Hg in continuous flow) [11]. Later, Gaset et al. patented the production of glycidol (72% yield in 1 h) at low pressure (3.5 kPa) and 183 °C by heterogeneous catalysis, using zeolite-A and glycerol as co-reagent [12]. Recently, Yuichiro et al. patented the process for obtaining glycidol using a homogeneous catalyst, sodium sulfate anhydrous, at 200 °C and low pressure (2.7 kPa), reaching yields of 80% after 6 h in the presence of a solvent containing no active hydrogen [13]. Ether-based solvents, saturated hydrocarbon-based solvents and aromatic hydrocarbon-based solvents would serve as solvents with

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non-active hydrogen; the absence of active hydrogen would help stabilize glycidol product [13], but their use would result in an economic and environmental challenge. In that case, the improvement stands the higher selectivity obtained in homogeneous media in contrast with Malkemus and Currier's, which could not suppress side reactions [11].

Current art is limited to reactions run at low pressure and with significant constraints in the nature of the solvent. Here, we report an effective process to transform glycerol carbonate into glycidol in dry media using a heterogeneous catalyst at significantly milder reaction conditions than those known in literature, and running at atmospheric pressure.

For that purpose, clean and eco-efficient methodologies that allow decreasing the amount of waste and a better use of energy are proposed. Thus, we report, for the first time, the use of microwave and ultrasound irradiation to carry out the liquid-phase synthesis of glycidol from glycerol carbonate. The reaction was run in the absence of any solvent under milder reaction conditions such as low temperature and atmospheric pressure than those reported previously. Thus, this work offers a practical alternative to conventional heating in traditional catalysis.

Some of these important alternative technologies are microwaves and ultrasonic irradiation. Both techniques provide a number of beneficial effects on the chemical reactivity that are not reproducible under conventional thermal activation. Microwave-assisted chemical reactions are accelerated because of selective absorption of microwave energy by polar molecules. The short reaction time, and expanded reaction range that is offered by microwave-assisted synthesis are suited to the increased demand in industry [14–17]. On the other hand, ultrasonic irradiation accelerates numerous catalytic reactions in both homogeneous and heterogeneous systems, reaching significant yield improvement [18–21]. The interaction between a suitable field of acoustic waves and a potentially reacting chemical system originate the phenomena known as sonochemical, through the intermediate phenomenon of the acoustic cavitation [21–23]. The acceleration of the reaction, the reduction of the induction period, and the enhancement of the catalyst efficiency are some of the beneficial effects that sonication has on the chemical reactivity [21,24]. In addition, the use of heterogeneous catalysts in dry media can contribute to improve the production process, eliminating or transforming unwanted and/or toxic byproducts avoiding the need for ulterior separation.

2. Experimental

2.1. Preparation of the catalysts and characterization

The catalyst containing 10 wt.% of Co_3O_4 nanoparticles on ZnO microparticles was prepared by a well-defined dry nanodispersion procedure [25–27]. The dry dispersion process consisted on shaking $\text{Co}_3\text{O}_4/\text{ZnO}$ mixtures with 1 mm ZrO_2 balls in a 60 cm³ nylon container for 5 min at 50 rpm using a tubular-type mixer. Pure micro-ZnO and nano- Co_3O_4 powders were also subject to the same mixing process to ensure that no structural disorder contributions occur in the mixing process. After that, ZnO and Co_3O_4 powders were dried at 110 °C for 2 h before dry mixing. The resulting materials were used as prepared (room-temperature, RT), denoted as RT-10CoZn.

The ZSM-5 catalyst, provided by Zeolyst International Company, was dried at 100 °C before used in the reaction. The particle size and morphology of the both catalysts were evaluated using secondary electrons images of Field Emission Scanning Electron Microscopy, FE-SEM (Hitachi S-4700). The surface area of the catalyst and the adsorption/desorption isotherm was determined with

a Micromeritics ASAP-2000 analyzer with N_2 as the adsorbate at –196 °C. The total acidity of the ZSM-5 zeolite was determined by ammonia chemisorption with a Micromeritics ASAP 2010C V.3.01 instrument.

2.2. Reaction procedure

2.2.1. Conventional heat-induced reaction

Glycerol carbonate (15 mmol) was heated in a batch reactor at 150 °C while stirring and in the absence of any solvent. After 5 min, the catalyst (5 wt.%) was added and the reaction time started. The reaction was followed using a HP5890 gas chromatograph (GC) equipped with a 50 m long Ultra 2 – 5% phenyl methyl siloxane capillary column and a flame ionization detector (FID). Blank reaction under conventional thermal activation in absence of catalyst resulted in negligible yield values.

2.2.2. Ultrasound-activated reaction

Glycerol carbonate (15 mmol) without any solvent was suspended in a quartz flask into the ultrasonic bath. The ultrasonic equipment is an Ultrasonic Bath-HD provided with a heating system (75 W heater power, 50–60 °C maximum temperature reached), 40 Hz of frequency with an ultrasonic generator of 120 W. After 5 min, the catalyst (5 wt.%) was added and the reaction time started. The reaction was followed in the same way as in the previous paragraph. Blank reaction under ultrasound activation in absence of catalyst resulted in negligible yield values.

2.2.3. Microwave-activated reaction

The microwave-assisted reaction was performed in a Multi-mode MicroSYNTH LabStation equipment fitted with magnetic stirring and a PRO-6 Rotor reactor vessel. An IR sensor controlled temperature during reaction. Microwave-activated reactions were carried out in Milestone quartz vessels, with 5 mL capacity. These vessels were provided with a pressure relief valve that vents the excess pressure and reseals, with no loss of reagents.

Glycerol carbonate (15 mmol) without any solvent and 5% in weight of catalyst were blended in a quartz vessel. The mixture was introduced in the microwave equipment and with modulated irradiated power (up to 200 W) to reach 150 °C, with 10 °C/min heating ramp. The reactor vessel was held in the microwave for 30 min under continuous stirring at such temperature. After cooling, the reaction products were extracted and filtered. The reaction was followed as described above. Blank reaction under microwave activation in absence of catalyst resulted in negligible yield values.

3. Results and discussion

3.1. Characterization of the catalysts

Field Emission Scanning Electron Microscopy (FE-SEM) was used to study further details of the ZSM-5 catalyst, Fig. 1. Fig. 1(a) shows a low-magnification image of the ZSM-5 catalyst. From Fig. 1(a), the ZSM-5 catalyst structure can be clearly observed. The zeolite ZSM-5 is an aggregation of submicron particles, which forms round-shaped agglomerates of ~10 µm, Fig. 1(a). To investigate also the submicron particles morphology of the ZSM-5 catalyst, a higher resolution was employed, Fig. 1(b and c). Thus, the zeolite ZSM-5 particles possess an irregular morphology with ca. 250 nm in size, see Fig. 1(c).

Fig. 1(d) shows the FE-SEM image of the RT-10CoZn catalyst. Fig. 1(e and f). From Fig. 1(e and f), the ZCo10-Nps structure can be clearly observed. Isolated Co_3O_4 nanoparticles are highly and uniformly mono-dispersed on the ZnO support with an average size of about 35–40 nm and of 0.5–1.0 µm, respectively. The FE-SEM micrograph also shows the typical ZnO-support morphology, which

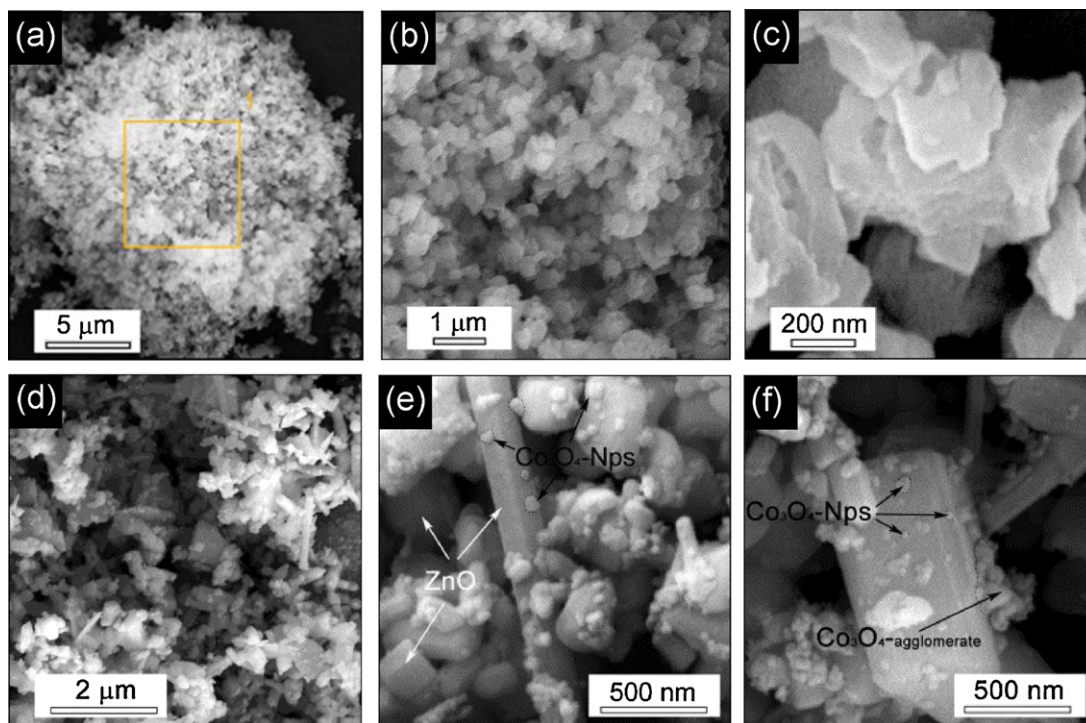


Fig. 1. Morphological characterizations of the catalysts through Field Emission Scanning Electron Microscopy Micrograph: (a–c) ZSM-5 series; (d–f) RT-10CoZn. The figures (b) and (c) show details of ZSM-5 catalyst; (e–f) magnified SEM images where it can be observed the ZnO-support microparticles and Co_3O_4 spherical respectively.

consisting mainly in rod-like particles with well-defined morphology, Fig. 1(e). Furthermore, the morphology of Co_3O_4 nanoparticles is formed to small spherical particles with 30–40 nm in sizes see Fig. 1(e and f). The dispersion and greater adherence of nanoparticles could indicate the appearance of $\text{Co}_3\text{O}_4/\text{ZnO}$ interfaces at room temperature between these materials, due to the high initial reactivity of the Co_3O_4 and of the ZnO components. Dispersed individual nanoparticles dominate below 10 wt.% Co_3O_4 , but some agglomerates become apparent, see Fig. 1(f). This means that a dispersion limit of Co_3O_4 nanoparticles has been reached.

The N_2 adsorption–desorption isotherms of the two catalyst series were employed. The corresponding textural characteristics are reported in Table 1. In both series, the isotherms are mainly of type I according to the IUPAC characteristics of microporous solids. The isotherm hysteresis loop is of the H3 type, associated with agglomerates of particles that present pores with form of split, where capillary condensation happens. The BET area values of the ZSM-5 catalyst series are estimated at $362 \text{ m}^2/\text{g}$ (Table 1). As well the external area is calculated by means of t -plot method with a value of $118 \text{ m}^2/\text{g}$. The total acidity determined by ammonia chemisorption is $12.7 \text{ cm}^3/\text{g}$.

The opposite behavior is observed for the RT-10CoZn series; the BET surface area of the series decreases upon nanodispersion of Co_3O_4 nanoparticles (ca. $35 \text{ m}^2/\text{g}$) on ZnO microparticles (ca. $2.8 \text{ m}^2/\text{g}$). Thus, the BET surface area of the RT-10CoZn sample is ca. $5 \text{ m}^2/\text{g}$ (Table 1). These opposing trends indicate that the interaction during catalytic reaction will be totally different in both cases. To sum up, the most distinctive feature of the zeolite series is the high specific area presented, as compared to a lower specific area found for materials obtained by dry-nanodispersion method.

3.2. Synthesis of glycidol

To date, there are only a few studies about the synthesis of glycidol from glycerol carbonate [11–13]. Therefore, there is no well-established reaction mechanism yet. Mounloungui et al.,

postulated a possible reaction mechanism for this reaction. This mechanism was based on the polymerization of glycerol carbonate to poly-(glyceril-1,2-dicarbonate), which would then release a carbon dioxide forming glycidol (Scheme 1) [28].

3.2.1. Thermal activation

The results obtained over both catalysts, ZSM-5 zeolite and RT-10CoZn show that under conventional thermal activation in a batch discontinuous reactor (Fig. 2), both catalysts achieved similar conversion values, close to 35% (150°C , 23 h) but different selectivity to glycidol; with is close to 100% for the ZSM-5 zeolite and near 60% selectivity for RT-10CoZn catalyst. Ethers from the break in the chain of the poly-glycerol-1,2-carbonate polymer were the other reaction products obtained in the former catalysts, which confirms the reaction mechanism proposed by Mouloungui and Yoo [28].

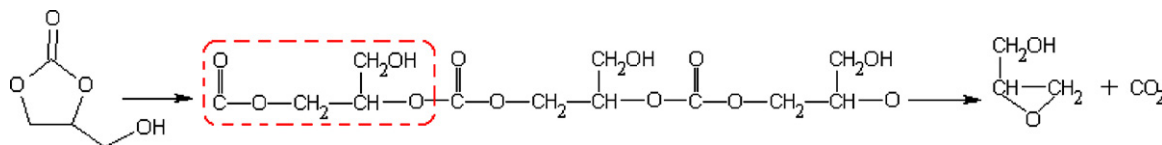
3.2.2. Ultrasonic activation

The use of ultrasonic activation in the reaction at nearly 60°C affords higher conversion values than under conventional thermal activation, 48 vs. 44% on ZSM-5 zeolite and on RT-10CoZn, respectively, and RT-10CoZn delivers total selectivity to glycidol (Fig. 2). The need of just one fourth of reaction time (7 h vs. 23 h) than under conventional thermal activation and the much lower temperature (ca. 60°C vs. 150°C) results is an important indicator of the intensification of this process. These data show that ultrasonic chemical activation clearly affects the course of the reaction increasing its energy efficiency. The lower reaction temperatures achieved under ultrasound activation makes the bond breaking of the poly-glycerol-1,2-carbonate chain more difficult. This fact would explain the lowest selectivity obtained for the ZSM-5 catalyst under ultrasound activation. The fact that ZSM-5 material possesses a large fraction of its area as internal may hamper bubbles implosion upon ultrasonic irradiation, thus accounting for lower efficiency of this activation. This is not the case of RT-10ZnCo catalyst, which increases its selectivity.

Table 1
Textural properties of the ZSM-5 and RT-10CoZn catalysts.

Catalyst	S_{BET} (m ² /g)	S_{ext} (t-plot) (m ² /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	V_{total} (cm ³ /g)
ZSM-5	362	118	0.178	0.063	0.242
RT-10CoZn	4.8	0.7	0.002	0.029	0.032

Micropore: $\phi < 2$ nm; mesopore $2 < \phi < 50$ nm.



Scheme 1. Reaction mechanism for the synthesis of glycidol from glycerol carbonate.

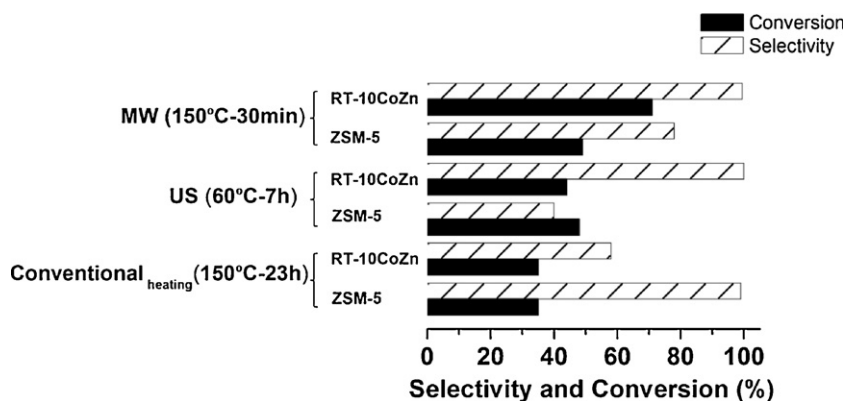


Fig. 2. Catalytic performance of both ZSM-5 and RT-10CoZn catalysts in the synthesis of glycidol from glycerol carbonate in dry media under conventional thermal activation, ultrasonic activation and microwave activation.

3.2.3. Microwave activation

Fig. 2 shows that microwave activation (150 °C, 200 W, 30 min) is particularly effective for this reaction. RT-10ZnCo reaches 71% conversion with total selectivity to glycidol in half an hour. The efficient absorption of microwaves by the Co_3O_4 nanoparticles dispersed on ZnO microparticles [29,30], could be further enhanced by the occurrence of magnetism at the interface between Co_3O_4 and ZnO particles [31]. This catalyst delivers the best performance in the shortest reaction time (30 min vs. 6–7 h under ultrasonic activation and vs. 23 h). That may account for the worst performance of ZSM-5 catalyst (49% conversion and 78% selectivity). Furthermore, microwave irradiation of ZSM-5 leads to an accelerated zeolite dealumination than under other heating methods, which affects its surface and acidic properties [32,33].

3.2.3.1. Relevance of these results. The results obtained in the synthesis of glycidol from glycerol carbonate demonstrate that alternative activation methods such as ultrasound and microwaves affect the course of the reaction, modifying selectivity trends. In fact, the results presented here deliver significant improvements compared with current art. Compared with data presented in the literature (Table 2), the systems reported here demand much milder operation conditions (temperature and time) and simpler experimental conditions (atmospheric pressure and dry media) to reach much higher conversion for glycerol carbonate (up to ca. 70%) and much higher (total) selectivity to glycidol. Mounloungui et al. run this reaction at low pressure (2.71 kPa) and 200 °C reaching of 80% yield in six hours using a zeolite as catalyst (Table 2) [12]. In this work, we run the reaction at atmospheric pressure, with a heterogeneous catalyst, in dry media at 150 °C needing significantly less time: 30 min vs. 360 min. These changes lead to remarkable process intensification through a much more efficient

Table 2

Comparison of the results obtained in this work for the synthesis of glycidol from glycerol carbonate with those obtained by other authors.

	Mouloungui et al. [12,28]	This work
Heterogeneous catalyst	Zeolite A	RT-10CoZn
Reaction conditions	200 °C Low pressure (2.71 kPa) Glycerol solvent	MW ^a 150 °C Atmospheric pressure Dry media
Reaction time (min)	360	30
Conversion (%)	88	71
Selectivity (%)	98	>99

^a MW, microwave activation.

use of energy and materials. In addition to use milder reaction conditions, atmospheric pressure and dry media, we report an economic heterogeneous catalyst that can be easily prepared.

4. Conclusions

This work presents the research to intensify the synthesis of glycidol from glycerol carbonate in dry media, which results in a more efficient use of energy and materials (no solvent, heterogeneous catalyst and total selectivity). Thus, we report, for the first time, the use of microwave and ultrasonic irradiation to carry out the liquid-phase synthesis of glycidol from glycerol carbonate in absence of any solvent using a heterogeneous economic micro-ZnO supported nano- Co_3O_4 particles catalysts, which operate under milder reaction conditions (150 °C) that previously reported and at atmospheric pressure. Thus, this work offers a practical alternative to conventional heating in traditional catalysis and brings important improvements in the search of new routes to transform

glycerol and its derivatives in high added value chemicals and less environmental impact.

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